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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

From the results obtained in this study, it is apparent that Al-Cu-Li alloys are amenable to electrochemical extraction. A combination of extracting to a powder and x-ray diffractometer scanning should produce optimum results. Confirmation of this should then allow a determination of the effects of minor alloying additions on the precipitated phases in Al-Cu-Li and Al-Li alloys, an evaluation of the sequential development of these phases during age-hardening as a function of both lithium content and aging temperature, and an assessment of the influence of the precipitates, as well as insolubles and dispersoids, on fracture toughness.

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FINAL REPORT

A Fundamental Study of Precipitates and the Influence of their

Crystal Structure on the Strength of Age-Hardenable

Aluminum-Lithium Alloys

Marion L. Shepard
Franklin H. Cocks

Department of Mechanical Engineering
and Materials Science
Duke University
Durham, NC 27706

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Introduction

Precipitated intermetallic compounds have long been of critical importance in determining the properties of a very large number of aluminum alloys. Because of the central role such precipitates play, the study of their structure and composition has widespread application in aluminum alloy metallurgy. In the past, the study of most aluminum alloy precipitates has of necessity been carried out primarily through the in situ X-ray methods first developed by Guinier [1] and Preston [2]. It is possible to selectively remove $MnAl_6$ second phase particles by anodic dissolution of Al-Mn alloys in strong acids [3], but such acids are usually found to dissolve both matrix and precipitate constituents. More recently the electron microscope and extraction-replica methods for the study of isolated precipitate particles have been developed [4,5]. These methods, however, cannot readily be used to produce the quantities of precipitates required for X-ray diffraction experiments or normal chemical analysis. X-ray, rather than electron microscope methods are needed, of course, if accurate lattice parameter measurements are to be made.

A variety of experimental procedures have been developed for the extraction of second phases from steels and nickel-based alloys. Many inclusions and intermetallic compounds, including simple and complex carbides, oxides, nitrides, and sulphides have been extracted from steels, for example, by the cold nitric acid method [6]. Separation of phases from nickel-based alloys has also been conducted for many years [7-11]. Carbide phases found in such alloys can be simply and quantitatively extracted because their bonding is sufficiently different from that of the fcc solid solution matrix, γ, and the ordered fcc precipitate, γ'. By using anodic dissolution techniques, separation of γ', whose composition, structure, and bonding are similar to the γ matrix, has been successfully accomplished.

Generally, galvanostatic or potentiostatic dissolution techniques have proven more satisfactory than simple chemical methods [12]. A recent anodic dissolution technique has been used, for example, to extract both precipitates and inclusions from a wide variety of steels with either low or high carbon content as well as with both low and high alloy content, including stainless steels [13]. This technique utilizes an NaCl EDTA (ethylenediaminetetraacetic acid) solution as an electrolyte and current densities of approximately 50mA/cm^2 to quantitatively extract the second phases. No equivalent anodic or electrochemical methods appear to have been applied to the selective dissolution of aluminum alloys in organic media. Based on a chemical process proposed by Honda and Hirokawa [14], an electrochemical extraction method based on an organic medium specifically applicable to age-hardenable aluminum alloys, which allows the specific extraction of second phase substances from aluminum base alloys [15], has now been developed. In this present work, the aim was to apply this method specifically to Al-Li and Al-Cu-Li alloys.

Experimental Procedure

A quantity of laboratory-produced aluminum alloy 2020 was obtained from Alcoa Research Laboratories and spectrochemically analyzed. The nominal and analyzed compositions are given in Table 1. Samples approximately 2 cm x 2 cm x 1 mm thick were cut, ground flat on 240-grit SiC paper, solution heat treated for 3 hours at 525°C $\pm$ 5°C, and water quenched. Aging heat treatments were carried out in fused KNO$_3$-LiNO$_3$ salts for 24 hours at 350°C $\pm$ 4°C and 22 hours at 400°C $\pm$ 4°C. These overaged conditions were chosen to allow the formation of large precipitates which give sharp diffraction profiles.

The electrochemical extraction process [15] consisted of immersing a sample in a solution of 10 gm 8-hydroxyquinoline, 40 gm benzoic acid, 40 ml chloroform, and 110 ml methanol, and depassivating the sample surface with an anodic current of

approximately $10mA/cm^2$ at 35V using a pure Al wire as the counter-electrode. Once the reaction began vigorously (~ 1 minute), the sample was disconnected from the current source and allowed to rest on the bottom of the beaker. In this way, precipitate particles were less likely to be dislodged from the sample surface as the aluminum matrix went into solution. Upon the formation of a black surface layer precipitates adhering to the partially dissolved aluminum substrate, the samples were removed from the complexing solution and gently rinsed with methanol. Subsequently, the samples were mounted on a diffractometer stage and x-ray data were taken. All diffractometer scans utilized Cu $K\alpha$ radiation and were made at 0.4 degrees/minute over the range $10° \leq 2\theta \leq 147°$.

Results and Discussion

X-ray diffraction data from two samples prepared by the method previously described are shown in Table 2. The strong lines due to the aluminum matrix have been omitted for clarity. Identification of lines in these diffraction patterns was based on a search of the literature on crystallography of phases present in the alloy systems Al-Cu-Li [16-18]. The d-spacings of compounds reported to have been observed in Al-Cu-Li alloys are given in Table 3, along with hkl indices and relative line intensities where available.

Comparison of Tables 2 and 3 show that T_B phase (Al_7Cu_4Li) and T_1 phase (Al_2CuLi) were found in both samples, i.e., those aged at 350°C and at 400°C. Due to the minimal number of lines found, however, another sample was aged at 350°C and extracted according to the original procedure [15]. By contrast with the method used to produce the previously described samples, this sample, identified as Sample C in Table 2, was extracted to produce a powder. The powder was washed and centrifuged several times and dried prior to obtaining Debye-Scherrer x-ray data. It can be seen that many additional T_B and T_1 lines were found. The Cu lines are believed to indicate that Cu was present as an artifact of the complexing process.

The results obtained thus far suggest that phase identification in Al-Cu-Li alloys can be made by the electrochemical extraction and x-ray analysis process described. In order to increase the number of lines obtained and, at the same time, to obtain direct evidence of line intensity and peak broadening afforded by the diffractometer tracings as compared to Debye-Scherrer powder patterns, sample C will be x-rayed on the diffractometer.

Conclusions

It is apparent that Al-Cu-Li alloys are amenable to electrochemical extraction. A combination of extracting to a powder and x-ray diffractometer scanning should produce optimum results. Confirmation of this should then allow a determination of the effects of minor alloying additions on the precipitated phases in Al-Cu-Li and Al-Li alloys, an evaluation of the sequential development of these phases during age-hardening as a function of both lithium content and aging temperature, and an assessment of the influence of the precipitates, as well as insolubles and dispersoids, on fracture toughness.

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Table 1: Composition of Al 2020

	Cu	Li	Mn	Fe	Si	Cd	Al
Nominal*	4.5	1.3	0.5	$\leq$0.25	$\leq$0.30	0.20	Remainder
Measured	4.07	1.08	0.33	0.091	0.22	0.19	Remainder

*T. H. Saunders, "Factors Influencing Fracture Toughness and Other Properties of Aluminum-Lithium Alloys," Semi-Annual Report, June-December 1976, Contract No. N62265-76-C-0271, to Naval Air Systems Command, by Physical Metallurgy Div., Alcoa Laboratories.

Table 2. Observed X-ray Lines

Sample A
Aging Treatment: 350°C, 24 hr
X-ray Method: Diffractometer
Sample Preparation: Particles adhering to Al matrix surface, rinsed and dried

d,Å	I/I₁	Identification
3.363	56	T_B 111 (3.368)
2.151	8	T_1 200 (2.145)
2.117	10	
2.060	100	T_B 220 (2.062)
1.987	10	
1.757	19	T_B 311 (1.759)
1.459	8	T_B 400 (1.458)
1.455	8	
1.453	8	
1.218	58	
1.190	10	T_B 224 (1.191)

Sample B
Aging Treatment: 400°C, 22 hr
X-ray Method: Diffractometer
Sample Preparation: Particles adhering to Al matrix surface, rinsed and dried

d,Å	I/I₁	Identification
3.371	60	T_B 111 (3.368)
2.152	40	T_1 200 (2.145)
2.062	100	T_B 200 (2.062)
1.956	40	T_1 202 (1.949)

Sample C
Aging Treatment: 350°C, 24 hr
X-ray Method: Debye-Scherer Camera
Sample Preparation: Powder extracted from sample, washed and dried

d,Å	I/I₁	Identification
7.49	30	T_1 002 (4.69)
4.68	10	T_B 111 (3.368)
3.37	70	
2.45	56	
2.15	5	T_1 200 (2.145)
2.10	100	Cu 111 (2.088)
2.06	90	T_B 220 (2.062)
1.95	10	T_1 202 (1.949)
1.81	25	Cu 200 (1.808)
1.76	30	T_B 311 (1.759)
1.46	20	T_B 400 (1.458)
1.34	10	T_B 331 (1.338)
1.28	26	Cu 220 (1.278)
1.196	30	T_B 224 (1.191)
1.12	5	T_B 333 (1.123)
1.09	46	Cu 311 (1.0900)
1.03	5	T_B 404 (1.031)
0.92	10	T_B 206 (0.922)
0.78	30Kα₁	T_B 246 (0.779)

Table 3:

d-Spacings for Phases Reported in Commercial Al 2020

Compound	d,Å	I/I_1	hkl	Compound	d,Å	I/I_1	hkl
$T_B = Al_7Cu_4Li$[16]	3.368		111	$'=Al_3Li$[17]	2.835		110
	2.917		200		2.315		111
Cubic, CaF_2-type	2.062		220	Cubic,	2.005		002
a=5.833Å	1.759		311	Cu_3Au-type	1.793		210
	1.684		222	(L_{12} type)	1.637		211
	1.458		400	a= 4.01Å	1.418		220
	1.338		331		1.337		221,300
	1.304		420		1.268		310
	1.191		224		1.209		113
	1.123		333		1.158		222
	1.031		404		1.003		400
	0.922		206		0.920		133
	0.779		246		0.819		224
					0.772		333
$T_1 = Al_2CuLi$[16]	4.69	S	002				
	4.31	M	100	Al_7Cu_2Fe[18]	7.405	10*	002
Hexagonal,	3.90	M	101		5.823	10	101
	3.15	M	102	hkl for	3.893	20	103
a=4.97Å,c=9.35Å	2.333	MS	004	predicted	3.703	100	004
	2.187	M	112	reflections	2.853	10	114
	2.145	S	200	and I/I_1	2.782	6	211
	2.047	M	104	taken from	2.683	70	105
	1.949	S	202	isomorphous	2.645	10	212
	1.579	M	204	compound,	2.239	6	220
	1.367	M	302	$KCa_4(Si_4O_{10})F.8H_2O$	2.162	10	116
	1.333	M	214		2.090	6	301
	1.320	M	116	$D_{4H}^6 = Pr/mnc$	2.047	30	215
	1.240	M	220	type	2.007	8	107
	1.199	M	222	Tetragonal,	1.861	6	216
	1.096	M	224	a=6.333Å	1.856	16	313
	1.075	M	400	c=14.810Å	1.659	10	315
	1.062	M	314		1.587	10	324
	1.047	M	402		1.416	6	420

Weak lines omitted